PATENT SPECIFICATION

(11) 1 544 155

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(21) Application No. 35483/77 (22) Filed 24 Aug. 1977
(44) Complete Specification published 11 April 1979
(51) INT CL² B32B 23/00 9/02//A22C 11/00
(52) Index at acceptance
B2E 1747 400T 402S 423T 429T M
A2B 19D1 19X1 19X2

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(54) METHOD FOR PREPARING PROTEIN-COATED FILM

(71) We, FUJI OIL COMPANY, LIMITED, a Japanese Body Corporate, of No. 6-1, Hachiman-cho, Minami-ku, Osaka-shi, Osaka-fu, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a method for preparing protein-coated films. More particularly, it relates to a method for preparing protein-coated films useful for packaging foodstuffs, by coating a protein-containing material on the surface of a regenerated cellulose film (i.e. Cellophane) and then drying.

The protein-coated films are particularly useful for packaging fish meat or animal meat paste products, such as ham-like paste products, sausage or boiled fish paste. That is, the fish meat or animal meat paste products may be covered with the protein-coated film so that the protein coating layer faces the paste products, and the resultant may be subjected to a heat treatment in the wet state whereby the coated protein is caused to migrate to the surface of the paste products (hereinafter, this treatment is referred to as "migration treatment"), and then the film may be peeled off. Paste products made in this way are hereinafter exemplified having excellent glossy surfaces and an improved shelf life.

Various studies have hitherto been done on methods for coating natural high molecular materials such as proteins or polysaccharides onto various films. However, these natural high molecular materials are predominantly used as adhesives for laminate films, or for preventing frictional damage of surface of synthetic resin films or for improving the printability of the resin films, and they are also used for producing photographic films.

Also, there are some reports that some edible coating films have been applied to foodstuffs. For instance, it is described in Japanese Patent Publication No. 18481/1961 that a packaging film is prepared by coating a water soluble adhesive (a coating agent) comprising a member selected from starches, casein, sodium alginate, polyvinyl alcohol or carboxy methyl cellulose (CMC) and an appropriate antiseptic onto the inner face of the film and drying the product, and that the packaging film thus prepared is applied to processed meat products, and the resultant is boiled whereby the coating layer is caused to migrate to the surface of the processed meat products, by which the products are improved in resistance to putrefraction and also in the glossiness of their surfaces. However, when using a conventional film coated with an edible substance, it is difficult to make the coating layer migrate to the surface of the processed meat product. For instance, the migration treatment may require as long a time as 2.5 hours at 90°C. Thus, the conventional migration treatment is carried out at a high temperature for a long period of time, during which gases such as steam are produced within the package, and hence, the pressure inside the package is increased, by which the film is stretched or expanded and is occasionally broken, and decreased yield of the final product or other defects are induced. It is necessary to simplify the migration treatment not only to increase the yield of the product but also to simplify the processes in the automatic or continuous production of paste products, to decrease the fuel cost, etc.

When a conventional film coated with edible substances is used and a simplified migration treatment is carried out by using, for example, boiling water at 80°C for 50 minutes, the migration of the coating layer can not be adequately performed, and hence, when the film is peeled off, there is observed the so-called "stringing" phenomenon between the film and the coating layer, owing to the high viscosity of the coating layer, and occasionally the migration is not uniform and the coating layer is partially retained on the film to give inferior products having uneven surfaces.

According to the present invention there is provided a method for making a protein-

coated film, which method comprises coating a regenerated cellulose film with an aqueous dispersion containing a polyhydric alcohol, soy protein, at least part of which is denatured, and optionally other protein and/or one or more polysaccharides, the dispersion containing at least 40% by weight of soy protein based on the total weight of protein and, if present, polysaccharide, and drying the coating.

The desired protein-coated films can therefore be prepared by using an aqueous dispersion containing a soy protein having high gelling properties as a coating agent, and coating the aqueous dispersion on the surface of regenerated cellulose film and drying the resultant, wherein at least a part of the soy protein is denatured with heat before the dispersion is coated on the Cellophane.

The aqueous dispersion used as a coating agent in the present invention comprises soy protein making up at least 40% by weight of the solid components and a polyhydric alcohol (as a plasticizer), wherein one or more other proteins and/or polysaccharides may be incorporated as solid components. The aqueous dispersion should contain at least 40% by weight of the protein and polysaccharides of soy protein. When the proportion of soy protein in the solid components is less than 40% by weight, the gelation of the coating layer is inhibited, and when the coated film prepared from such an aqueous dispersion containing less than 40% by weight based on the total solids of soy protein is subjected to the migration treatment using a boiling water at 80°C for 50 minutes, the coating layer does not sufficiently migrate to the surface of the foodstuffs, and hence, uneven migration occurs which results in undesirable lowering of the glossiness of the surface of products. Thus, the protein and polysaccharides of the aqueous dispersion are composed of 40 to 100% by weight of soy protein and 60 to 0% by weight of one or more other proteins and/or polysaccharides.

Another feature of the present invention is that at least a part of the soy protein contained in the coating dispersion is denatured, preferably, with heat. The starting soy protein may be a denatured protein or a natural protein (i.e. soy protein being not denatured). However, when a natural soy protein is used, it is preferable to denature at least partially the natural soy protein at any stage before coating the aqueous dispersion onto the Cellophane. Denaturation may be carried out, for instance, by heating the aqueous dispersion at about 80°C for about 10 minutes. When an aqueous dispersion containing soy protein which is entirely undenatured is coated on the cellulose film, the coating layer is too densely adhered to the film, and hence, when the film is peeled off after the migration treatment, the balance between the adhesion forces between the film, the coating layer and the paste product and the strength of the coating layer is lost. This results in the occurrence of uneven migration of the coating layer and inferior glossiness of the surface of the final products. Thus, when natural soy protein is used for the preparation of the aqeous dispersion, it is important to denature at least a part of the soy protein before the coating of the aqueous dispersion in order to decrease the adhesion force between the coating layer and the film and to give an excellent migration property to the coating layer. The soy protein may be denatured alone or in a mixture thereof with one or more other proteins and/or polysaccharides. The denaturation may be carried out at any pH range which the aqueous dispersion retains sufficiently in dispersed phase to be suitable for coating onto the cellulose film. The aqueous dispersion after denaturation of the soy protein is preferably in the pH range of 6 to 10. When the aqueous dispersion has a pH value of lower than 6, it loses homogeneity, and on the other hand, when it has a pH value of higher than 10, adhesion between the coating layer and the cellulose film is increased, and hence, the cellulose film can not uniformly be peeled off. When the pH value of the coating layer may not be lowered in the process after the protein-coated film is applied to foodstuffs e.g. when the foodstuffs are such as fish meat or animal meat paste products, it is preferable to regulate the pH value of the aqueous dispersion to let in the range of about 6 to 8, at which pH no difficulties arise when the foodstuffs treated with the coated film are eaten.

The polyhydric alcohols to be used as the plasticizer in the present invention include any edible polyhydric alcohol, such as glycerin, sorbitol, mannitol or propylene glycol, which may be used alone or in combination with one or more others. The polyhydric alcohol is suitably used in an amount of 10 to 40% by weight on the basis of total weight of the solid components such as proteins and polysaccharides. The incorporation of the plasticizer is effective for giving a softness to the coating layer, whereby the adhesion between the cellulose film and the coating layer and also the stability of the coated film are improved, and the coated film is made easy to handle and hence its workability in packaging of foodstuffs is highly improved. Moreover, incorporation of the plasticizer can give wetting properties to the coating agent and the surface of the Cellophane and hence workability in the coating step is also

improved. The wetting effect may be given by any other edible emulsifying agents, and hence, such other emulsifying agents may also be incorporated, but are not necessarily used because the desired wetting effect can be given by the polyhydric alcohol alone. The polyhydric alcohols are suitably used in an amount of 10 to 40% by weight on the basis of total weight of the solid components, and when the amount is less than 10% by weight, the coating layer does not show sufficient softness, and on the other hand, when the amount is more than 40% by weight, the coating layer shows an undesirable tackiness and also undesirably too high softness.

The soy protein is preferably a separated soybean protein containing 60% by weight or more of pure protein, which may be in any forms of liquid, paste, or dry powder form. Other proteins which may be used with the soy protein include casein, collagen and gelatin. Polysaccharides which may be incorporated with the soy protein or with a mixture of soy protein and other proteins include various starches and edible cellulose derivatives.

The concentration suitable for the aqueous dispersion depends on the viscosity of the dispersion which is effective on operability thereof and the thickness of the desired coating layer. The pH value of the aqueous dispersion may be regulated to lie in the range of 6 to 10. The viscosity of the aqueous dispersion is preferably in the range of 10 to 500 cps (measured at 20°C by a B type viscometer), more preferably 50 to 200 cps, for industrial application of the method. When the viscosity is lower than 10 cps, it is difficult to form continuous coating layer on the cellulose film, and on the other hand, when the viscosity is higher than 500 cps, the workability of the aqueous dispersion is undesirably lowered.

The aqueous dispersion may be applied to the Cellophane by conventional coating methods such as roll coating, or spray coating. The coating layer is preferably formed with an average dry thickness of about 3 to 100 μ. Even if the thickness of the coating layer is thinner than 3 μ, there may be obtained the desired protein-coated film having the desired effect, but when such a protein-coated film is applied to fish meat or animal meat paste products, it is occasionally difficult to make the coating layer migrate to the paste products owing to the inferior strength of the coating layer. On the other hand, when the thickness of the coating layer is thicker than 100 μ, the coating layer has a large resistance to flexing and hence it has an undesirable tendency to lose adhesion to the cellulose film on flexing during handling.

After coating the aqueous dispersion onto the cellulose film, the coated film is dried. Temperature for drying is preferably low enough to prevent too high denaturation of soy protein and to inhibit undesirable deformation and deterioration of the cellulose film. The temperature may usually be 80°C or lower, preferably 40 to 80°C depending on the thickness of the coating layer, the concentration of the aqueous dispersion, or other factors. If the denaturation of soy protein contained in the coating layer proceeds too far during this drying step, it undesirably results in incomplete migration of the coating layer in use.

The protein-coated film thus dried may then be formed into a bag, wherein the coated face of the film becomes the inner face. After or during the forming into the bag, foodstuffs, particularly fish meat or animal meat paste products such as ham-like paste products, sausage or boiled fish paste, may be filled into the protein-coated film bag. After the filling of the foodstuffs (i.e. paste products), the coating layer absorbs moisture contained in the surface and inner part of the paste products and swells. As a result, the coating layer tends to adhere to the surface of the paste products, and a part of denatured soy protein gel is impregnated into the crude surface of the paste products. The thus packed paste products may be subjected to the migration treatment by using a boiling water at 80°C for 50 minutes, whereby the soy protein contained in the coating layer is completely denatured and gelated and is migrated into the surface of the paste products, and further the soy protein impregnated into the crude surface of the paste products and also the proteins contained in the paste products are simultaneously completely denatured and gelated, which results in strong adhesion between the paste products and the coating layer.

Thereafter, the cellulose cover film is peeled off to give paste products covered completely with a protein-containing coating layer. The paste products produced hereinafter in the Examples after peeling off the cover film show an excellent shelf life, and it is found that undesirable decoloration of the surface owing to evaporation of moisture and oxidation and also undesirable lowering of flavor can effectively be prevented. The products have also an excellent surface glossiness.

The film used as the base film in the present invention includes any conventional regenerated cellulose film, which may be in any form e.g. sheet, tube or bag form. It may be a laminate of cellulose film with another film or sheet. Furthermore, the coating agent (aqueous dispersion) may contain

other ingredients, such as antiseptics or colorants.

The present invention is illustrated by the following Examples, but is not limited thereto.

Example 1

Soybean milk obtained by extracting defatted soybean with water was regulated at pH 4.5 with hydrochloric acid, and the resulting precipitates were dehydrated to give curds (solid components: 40% by weight). To the curds (20 parts by weight) was added water (30 parts by weight), and the mixture was regulated at pH 10 with sodium hydroxide to give an aqueous dispersion containing soy protein (solid components: 16% by weight). The aqueous dispersion was subjected to denaturation by heating at 140°C for 10 seconds with superheated steam. After cooling, water (16 parts by weight) was added thereto so that the solid components became about 12% by weight, and further glycerin (2 parts by weight) was added thereto. The mixture was agitated and then was defoamed. The aqueous dispersion thus prepared showed a viscosity of 150 cps at 20°C (measured by B type viscometer).

The aqueous dispersion was applied onto a Cellophane base film (thickness: 20 μ) in a thickness of 200 μ by a coater equipped with a doctor blade, and the coated Cellophane was continuously dried by passing through a hot air dryer at 60°C (retention time: 3 minutes). The protein-coated film thus prepared had a soy protein-coating layer of 38 μ in thickness, which coating layer was a yellowish, semi-transparent and uniform layer and had an excellent adhesion to the base film and had also an excellent softness and an excellent resistance against flexing.

The protein-coated film thus prepared was formed into a cylindrical shape (diameter: 30 mm) by adhering both ends thereof. For comparison purpose, Cellophane film having no coating layer was formed into a cylindrical shape likewise.

Separately, pork meat (1.7 kg), sodium chloride (30 g), starch (60 g) and cooled water (300 g) were mixed to give a starting paste for sausage. The paste was filled in the above-prepared cylindrical film, and then both ends thereof were sealed, and the resultant was subjected to heat treatment with a boiling water at 80°C for 50 minutes.

After cooling, the cylindrical film was peeled off, and the appearance of the sausage thus treated was observed.

In case of the protein-coated film, the protein-containing coating layer was completely migrated to the sausage when the base film is peeled off, and the film could easily be peeled off. Besides, the sausage covered by the protein-containing coating layer had a glossy appearance. On the other hand, in case of the film having no protein-coating layer, the film was hard to peel off, and the appearance of the sausage was not good.

After peeling off the film, both sausages were allowed to stand in a room at 20°C and a relative humidity of 60% for 24 hours, and then decrease of weight of the sausage owing to evaporation of moisture was measured. As the results, decrease of weight was merely 7% in case of the protein-coated film, but was 16% in case of the film having no coating layer.

Example 2

Commercially availabe soy protein powder (Fujipro-R made by Fuji Oil Company Ltd., 70 parts by weight) and sodium caseinate (30 parts by weight) were dispersed in water so that the solid components became 14% by weight, and thereto was added sorbitol (30 parts by weight). The mixture was regulated at pH 10 and was agitated and defoamed to give a coating agent (aqueous dispersion) having a viscosity of 180 cps (at 20°C, measured by B type viscometer).

The aqueous dispersion was applied to a Cellophane base film in the same manner as in Example 1, and the coated cellophane was continuously dried by passing through a hot air dryer at 60°C for 3 minutes. The protein-coated film thus prepared had a soy protein-containing coating layer of about 40 μ, and the base film was covered by the protein-containing coating layer having a uniform thickness and an excellent adhesion to the base film.

The protein-coated film thus prepared was formed into a cylindrical shape (diameter: 30 mm) and thereto was filled a fish paste prepared by mixing ground meat of pollack (1800 g), starch (80 g), sodium chloride (45 g) and water (500 g), and then both ends thereof were sealed. The sealed cylindrical film was allowed to stand at 30°C for one hour and then was heat-treated in a boiling water at 85°C for 20 minutes.

When the Cellophane base film was peeled off, the protein-containing coating layer was migrated completely to the surface of the boiled fish paste. The boiled fish paste thus prepared had an excellent glossy surface and good chewing feeling.

Example 3

Commercially available coarse granular cowhide collagen (10 parts by weight) was mixed with water (90 parts by weight) and thereto was added hydrochloric acid (0.25 part by weight). The mixture was allowed to stand at about 20°C for 24 hours, and thereby the mixture swelled. The resulting mixture was ground and regulated at pH 5.5.

The resulting coagulation product was separated and washed with water. This coagulation product (3 parts by weight in dry state) was mixed with the soy protein powder prepared in Example 2 (7 parts by weight) and thereto was added water so that the solid components became 14% by weight, and the mixture was regulated at pH 8, and thereto was further added glycerin (3 parts by weight). The mixture was agitated and defoamed to give an aqueous dispersion (coating agent) having a viscosity of 220 cps (at 20°C, measured by B type viscometer).

The aqueous dispersion was applied to a Cellophane base film and dried in the same manner as in Example 1 to give a protein-coated film having a protein-containing coating layer of about 40 μ in thickness. The protein-coated film had a uniform protein-containing coating layer and the adhesion between the coating layer and the base film was excellent. When the protein-coated film was flexed in dry state, no cracking or peeling was observed.

In the same manner as in Example 1, the protein-coated film was formed into a cylindrical shape and thereto was filled the starting paste for sausage, and the resultant was treated, likewise. When the base film was peeled off, the protein-containing coating layer was uniformly migrated to the surface of the sausage, and there was observed the same effect as in Example 1.

Example 4

Potato starch (5 parts by weight) was dissolved in water (45 parts by weight) by heating the mixture at 80°C with agitation. To the solution was added soy protein.

(Fujipro-R, made by Fuji Oil Company, Ltd., 5 parts by weight), and thereto was added water (26 parts by weight) so that the solid components became 14% by weight. After adding glycerin (3 parts by weight) thereto, the mixture was regulated at pH 10 with sodium hydroxide and then agitated to give a uniform aqueous dispersion, which was defoamed to give an aqueous dispersion having a viscosity of 62 cps (at 20°C, measured by B type viscometer).

The aqueous dispersion was applied to a Cellophane base film and dried in the same manner as in Example 1 to give a protein-coated film having a protein-containing coating layer of 50 μ in thickness. The film had a uniform, semitransparent coating layer having an excellent softness and adhesion.

In the same manner as in Example 1, the protein-coated film was formed into a cylindrical shape (diameter: 30 mm) and thereto was added the starting paste for sausage, and after sealing the ends of the cylindrical film, it was subjected to heat treatment, likewise, to give the desired sausage having excellent properties.

Example 5

Soybean milk obtained by extracting defatted soybean with water was regulated at pH 4.5 with hydrochloric acid, and the resulting precipitates were dehydrated to give curds (solid components: 40% by weight). To the curds (100 parts by weight) was added water (233 parts by weight), and the mixture was regulated at pH 7.0 with sodium hydroxide and was heated at 90°C for 20 minutes in order to denature the protein. After cooling, to the mixture was added aqueous gelatin solution (concentration: 12% by weight, 82.5 parts by weight) to give an aqueous dispersion which contained gelatin in the ratio of 20% by weight on the basis of total weight of the solid components. To the aqueous dispersion was added mannitol (15 parts by weight on the basis of total weight of the centrifuged and defoamed to give an aqueous dispersion having a viscosity of 120 cps (at 20°C, measured by B type viscometer).

By using the same device as in Example 1, the aqueous dispersion was applied to a Cellophane base film and was continuously dried by passing through a hot air dryer at 60°C for 3 minutes to give a protein-coated film having a uniform protein-containing coating layer of about 30 μ in thickness. This film had an excellent adhesion between the cellophane base film and the coating layer.

In the same manner as in Example 1, the protein-coated film was formed into a cylindrical shape (diameter: 30 mm) and thereto was filled the starting paste for sausage, and the resultant was heat-treated in a boiling water at 85°C for 20 minutes to give the desired sausage. By peeling off the cellophane base film, there was obtained a sausage having an excellent glossy surface.

Reference Example 1

To a solution of commercially available sodium caseinate in water (concentration: 16% by weight) was added glycerin (30% by weight on the basis of the weight of the caseinate), and the mixture was agitated and defoamed to give a solution having a viscosity of 30 cps at pH 7 (at 20°C, measured by B type viscometer).

The solution (coating agent) was applied to a Cellophane base film and dried in the same manner as in Example 1 to give a protein-coated film having a protein-containing coating layer of 40 μ in thickness. This film had an excellent adhesion, softness and also an excellent transparency.

In the same manner as in Example 1, the film was formed into a cylindrical shape

(diameter: 30 mm) and thereto was filled the starting paste for sausage, and the resultant was heat-treated in a boiling water at 80°C for 50 minutes. When the base film was peeled off, the protein-containing coating layer was not completely migrated to the surface of sausage, and there was observed stringing phenomenon between the cellophane base film and the surface of sausage due to the viscosity thereof, and the sausage thus prepared had no glossy surface, and was covered viscous membrance, which gave bad feeling as if the freshness of the product was extremely lowered.

Reference Example 2

Soybean milk obtained by extracting defatted soybean being not denatured with water was regulated at pH 4.5 with hydrochloric acid, and the resulting precipitates were dehydrated to give curds (solid components: 40% by weight). To the curds (20 parts by weight) was added water (30 parts by weight), and the mixture was regulated at pH 10.0 with sodium hydroxide to give a soy protein-containing aqueous dispersion (solid components: 16% by weight). To the dispersion was added glycerin (2 parts by weight), and the mixture was agitated and defoamed to give an aqueous dispersion having a viscosity of 150 cps (at 20°C, measured by B type viscometer).

In the same manner as in Example 1, the aqueous dispersion containing non-denatured soy protein was applied to a Cellophane base film and dried to give a protein-coated film having a protein-containing coating layer of 40 μ in thickness. This film had an excellent adhesion and softness and also an excellent transparency.

In the same manner as in Example 1, the film was formed into a cylindrical shape (diameter: 30 mm) and thereto was filled the starting paste for sausage, and the resultant was heat-treated in a boiling water at 80°C for 50 minutes. After cooling, the cellophane base film was peeled off. As the result, the coating layer was not completely migrated to the surface of sausage, and the sausage had an inferior glossiness, which might be owing to the incomplete migration of the coating layer due to the difference in the adhesion between the cellophane and the coating layer.

"Cellophane" and "Fujipro" are Registered Trade Marks.

"Fujipro R" is a soy protein which has been denatured by flash pasteurisation by heating in steam at 140°C for 5 seconds.

WHAT WE CLAIM IS:—

1. A method for making a protein-coated film, which method comprises coating a regenerated cellulose film with an aqueous dispersion containing a polyhydric alcohol, soy protein, at least part of which is denatured, and optionally other protein and/or one or more polysaccharides, the dispersion containing at least 40% by weight of soy protein based on the total weight of protein and, if present, polysaccharide, and drying the coating.

2. A method as claimed in Claim 1, wherein soy protein is the only protein present in the dispersion and no polysaccharide is present.

3. A method as claimed in Claim 1, wherein the aqueous dispersion contains one or more proteins other than soy protein and/or one or more polysaccharides, in addition to soy protein.

4. A method as claimed in Claim 3, wherein the aqueous dispersion contains casein, collagen or gelatin or a mixture of two or all of these.

5. A method as claimed in Claim 3 or Claim 4, wherein the aqueous dispersion contains starch and/or a cellulose derivative.

6. A method as claimed in any one of the preceding claims wherein the polyhydric alcohol is glycerin, sorbitol, mannitol or propylene glycol.

7. A method as claimed in any one of the preceding claims wherein the polyvalent alcohol is present in the range of 10 to 40% by weight based on the total weight of the solid components in the aqueous dispersion.

8. A method as claimed in any one of preceding claims wherein the aqueous dispersion has a viscosity of 10 to 500 cps.

9. A method as claimed in any one of the preceding claims wherein the aqueous dispersion has a pH value of 6 to 10.

10. A method as claimed in any one of the preceding claims wherein all the soy protein in the dispersion is denatured soy protein.

11. A method as claimed in Claim 10 wherein the aqueous dispersion is heated before coating on to the regenerated cellulose film in order to denature the soy protein.

12. A method as claimed in any one of the preceding claims wherein the protein-containing coating layer is formed with an average dry thickness of 3 to 100 μ.

13. A method as claimed in any one of the preceding claims wherein the drying of the coated film is carried out at a temperature of 80°C or lower.

14. A method as claimed in Claim 1 substantially as hereinbefore described in any one of Examples 1 to 5.

15. A protein coated film produced by a method claimed in any one of the preceding claims.

16. A body of foodstuff material

contained in a protein coated film as claimed in Claim 15.

17. A body of foodstuff material as claimed in Claim 16 wherein the foodstuff material is a meat or fish paste or is sausage meat.

18. A body of foodstuff material as claimed in Claim 16 substantially as hereinbefore described in any one of Examples 1 to 5.

19. A method for preparing a foodstuff which method comprises contacting the foodstuff with the protein coated face of a film as claimed in Claim 15 and heating the foodstuff and film to adhere the protein coating to the foodstuff, and removing the regenerated cellulose film from the foodstuff leaving the protein coating adhering thereto.

20. A method as claimed in Claim 19 wherein the foodstuff is introduced into a tube or bag of film as claimed in Claim 15 and is heated therein.

21. A method as claimed in Claim 20 comprising heating a body of food material as claimed in Claim 17.

22. A method as claimed in Claim 19 substantially as hereinbefore described in any one of Examples 1 to 5.

23. A foodstuff prepared by a method as claimed in any one of Claims 19 to 22.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1979
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.